# ISOLATION OF O-BENZOYLTOMBOSINE AND THE N-OXIDES OF KOPSININE AND PSEUDOKOPSININE

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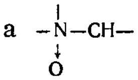
The present paper gives the results of a further investigation of the alkaloids of the epigeal part of Vinca erecta. From the nonphenolic fraction of the combined alkaloids of this plant collected on April 15-25, 1970, in the Surkhandar'ya oblast we have isolated two bases.

A base with the composition $C_{26}H_{26}N_2O_2$ (I), mp 255-256°C (ether), $[\alpha]_D^{20}+93°$ (c 0.3; chloroform) has been isolated for the first time. Its UV spectrum [$\lambda_{max}^{ethanol}$ 227, 281, 291 nm (log ε 4.48; 3.95 3.62)] is characteristic for indole derivatives. The IR spectrum shows absorption bands at (cm$^{-1}$) 3170 (=NH) and 1720 (ester carbonyl group). The NMR spectrum shows the presence of a $=CH-CH_3$ group (1.51 ppm, doublet; 5.40 ppm, quadruplet) and =NH group (8.39 ppm; singlet) and of nine aromatic protons (7.01-8.02 ppm). In the mass spectrum of (I) there are the peaks of ions with m/e 398 ($M^+$), 397, 293, 277, 276, 275, 263, 169, 168, 105. When (I) was saponified with a 10% ethanolic solution of KOH for 1.5 h, a base was obtained with mp 266-267°C which was identified from its $R_f$ values, IR spectrum, and mixed melting point as tomobsine. On the basis of an analysis of the UV, IR, mass, and NMR spectra and the results of saponification we assumed that substance (I) was O-benzoyltombosine. This was confirmed by the synthesis of (I) by the benzoylation of tombosine with benzoyl chloride in pyridine for 35 h.

Substance (II), $C_{21}H_{26}N_2O_3$, has mp 159-161°C (ethyl acetate). UV spectrum: $\lambda_{max}^{ethanol}$ 245, 297 nm (log ε 3.87, 3.47). IR spectrum, cm$^{-1}$: 3370 (=NH), 1730 ($-COOCH_3$), 755 (disubstituted benzene ring). In the NMR spectrum of (II) (δ scale, $CDCl_3$) there are the signals of the protons of a $-COOCH_3$ group (3.72 ppm, singlet), a Ar—H group (4 H, 6.50-7.05 ppm), and a  $-\overset{|}{\underset{\overset{\downarrow}{O}}{N}}-CH-$ group (8.11 ppm, doublet). The mass spectrum shows the peaks of ions with m/e 354, 338, 337, 336, 124, and 109. The similarity of the UV, IR and mass spectra of (II) and those of kopsinine, the difference in the peaks of their molecular ions by 16 units, and the high solubility in water permitted the assumption that base (II) is kopsinine N-oxide [1].

Substance (III), $C_{21}H_{26}N_2O_3$, with mp 186-188°C (ether) was isolated from the combined alkaloids of V. erecta collected in the Tashkent oblast in the fruit-bearing period [2]. The base is readily soluble in chloroform and methanol and less readily in ether. UV spectrum: $\lambda_{max}^{ethanol}$ 247, 301 nm (log ε 3.77, 3.43). The IR spectrum of (III) has the absorption bands of a 1,2-disubstituted benzene ring (760 cm$^{-1}$) and of a $CH_3COO-$ group (1730 cm$^{-1}$). The mass spectrum has the peaks of ions with m/e 338, 324, 279, 229, 170, and 135. The NMR spectrum of (III) has signals from the protons of a $CH_3-CH=$ group (0.86 ppm, doublet, J = 8 Hz), a $CH_3COO-$ group (3.61 ppm, singlet), the $C_{14}$ H atom (7.67 ppm, doublet, J = 8 Hz), and Ar—H (4 H, 6.55-7.00 ppm). From its UV, IR, and mass spectra and its high solubility in water and the presence in its NMR spectrum of the signal of the $C_{14}-H$ proton, which is characteristic of all indole alkaloids present in the N-oxide form, we assumed that the base (III) is pseudokopsinine N-oxide. The reduction of (III) with Zn/HCl yielded pseudokopsinine [3].

Thus, the two new bases that have been isolated from V. erecta have the structures of O-benzoyltombosine and pseudokopsinine N-oxide.

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